

CATALYSIS OF LIGNITE CHAR GASIFICATION BY VARIOUS
EXCHANGED CATIONS -- DEPENDENCE OF ACTIVITY ON REACTIVE ATMOSPHERE

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INTRODUCTION

We have previously reported reactivities of a vast spectrum of coal-derived chars in air (1), CO_2 (2), steam (3) and H_2 (4). In oxidizing atmospheres, char reactivity decreases with increase in the rank of the parent coal. In contrast, char reactivity in H_2 shows little dependence on rank of the coal precursor.

Because of the large reserves of lignites and subbituminous coals in the United States, they are potentially of importance in coal conversion processes. These coals contain significant amounts of carboxylic acid groups, where a fraction of the H^+ ions have been exchanged by different cations such as Na^+ , K^+ , and Ca^{++} , as a result of extended contact with ground water containing different salts. The higher reactivity of lignite and sub-bituminous coal chars in oxidizing atmospheres is thought to be due, at least in part, to the presence of exchangeable metal cations. Therefore, it is desirable to study the possible catalytic effect of different exchangeable cations present on the surfaces of these coals on subsequent char reactivity in different atmospheres. This paper describes the results of such a study.

EXPERIMENTAL

Char Preparation. A Darco (Texas) lignite (28x48 mesh) was demineralized by boiling with 10% HCl and subsequently with a 50-50 mixture of 50% HF -10% HCl . The carboxyl content of the demineralized coal was 2.4 mmoles/g. Schafer's method was used to effect cation-exchange (5). Demineralized (Dem) lignite was contacted with 0.10 molar solutions of sodium acetate, potassium acetate, calcium acetate, magnesium acetate and ferric nitrate. Approximately 0.3 mmoles of cation per gram of coal were exchanged from the various solutions in 24 hr. Ten levels of exchangeable calcium ions in the range 0.10 to 2.14 mmoles/g of coal were introduced by contacting the Dem coal with calcium acetate solutions varying in concentration from 0.04 to 2.0 molar for 24 hr.

Raw, Dem and cation-exchanged samples were carbonized in N_2 in a fluidized bed. In each case, the sample was heated up to 800°C at a rate of $10^\circ\text{C}/\text{min}$. Soak time at 800°C was 2 hr.

Reactivity Measurements

Reactivities of various char samples were measured in air (1 atm, 390°C), CO_2 (1 atm, 760°C), steam (1 atm, 650°C), H_2 (1 atm, 790°C), 50% CO -50% H_2 mixture (total pressure 1 atm, 790°C), N_2 - H_2O mixture (790°C), H_2 - H_2O mixture (790°C), H_2 - N_2 - H_2O mixture (790°C) and CO - H_2 - H_2O mixture (790°C). The partial pressure of water vapor in the last four mixtures (total pressure 1 atm) was 12.8 torr. This pressure was generated by bubbling the gas through deaerated distilled water thermostated at 15°C .

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Reactivity measurements in 1 atm steam were carried out in a fluid bed reactor. Weight losses occurring during gasification in the other atmospheres studied were monitored using a DuPont 951 TGA system in conjunction with a 990 Thermal Analyzer. Details of the experimental procedures for reactivity measurements have been described elsewhere (6).

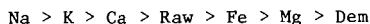
In the text, reactivity parameter, R , has been defined as:

$$R = \frac{1}{W_0} \cdot \frac{dW}{dt}$$

where W_0 is the initial char weight (daf) and dW/dt is the maximum rectilinear weight loss rate.

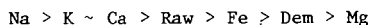
RESULTS AND DISCUSSION

Burn-off versus time plots for various char samples reacted in air are shown in Figure 1. The Dem char is significantly less reactive than the raw char. This has previously been attributed to the loss of catalytic inorganic matter upon demineralization (6). The following order of reactivities is observed for chars produced from raw, Dem and cation-exchanged samples:

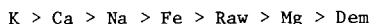


These results clearly show that the replacement of surface H^+ ions of carboxylic acid groups present on the surface of Dem lignite by metal cations increases the reactivity of the chars produced, but the extent of the increase is markedly dependent upon the nature of the cation. The higher reactivity of the char produced from the raw lignite compared to the iron and magnesium containing chars is thought to be due to the presence of catalytically active calcium ions in the raw lignite.

The following order of reactivities for various char samples was observed for the reaction in CO_2 :



and in steam:



Even though the $C-O_2$, $C-CO_2$ and $C-H_2O$ reactions all involve an intermediate oxygen transfer step followed by a gasification step, the order of reactivities of chars produced from different cation-exchanged samples is not the same in the three atmospheres. This shows the high specificity of different catalytic species.

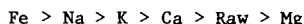
For the various calcium containing chars, the reactivity parameter in air, CO_2 and steam increased linearly with increase in the amount of calcium present in the char. Furthermore, normalized reactivities of these chars in the three oxidizing atmospheres were essentially the same.

Burn-off plots for various char samples in H_2 are shown in Figure 2. The order of reactivities of various samples in H_2 is markedly different from that observed in the three oxidizing atmospheres. Below 45% burn-off, sodium is the most effective hydrogasification catalyst; whereas at higher burn-offs iron is a better catalyst. It is noteworthy that even though calcium and potassium are excellent oxidation catalysts, chars containing these species are much less reactive in H_2 than the raw char. In fact, for the various calcium-containing

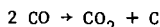
samples reactivity in H_2 decreased monotonically with increase in calcium loading.

Two extreme cases of the effect of H_2 addition to steam on char reactivity are illustrated by the plots in Figures 3 and 4. At one extreme, for the raw char (Figure 3), which has calcium as the major inorganic impurity, gasification is more rapid in wet N_2 than in wet H_2 . At the other extreme, the char produced from the iron exchanged sample has a higher reactivity in wet H_2 than in wet N_2 (Figure 4). It is known that in the elemental form iron is a good oxidation catalyst but in the oxide form it is a poor catalyst (7). In the present study, when the iron-containing char is reacted with wet H_2 , the percentage of H_2 in the mixture is sufficient to keep iron in the reduced state.

In the $CO-H_2$ mixture, chars produced from raw and Na, K, Ca and Mg exchanged samples showed little or no weight loss. However, in the $CO-H_2-H_2O$ mixture small but finite gasification rates were observed and the order of reactivity for various samples was:



Results for the iron-containing char were unique (Figure 5). In the $CO-H_2-H_2O$ mixture, the gasification rate is significantly lower than in N_2-H_2O or $N_2-H_2-H_2O$ mixtures. Further, in the dry $CO-H_2$ mixture, after a slight initial weight loss, there is a rapid continuous increase in weight. This increase is attributed to the disproportionation of CO:



For this reaction, iron is an excellent catalyst but is gradually deactivated due to the formation of cementite (8). In this study, the amount of H_2 in the $CO-H_2$ mixture is sufficient to keep iron in the catalytically active form, that is as elemental iron. Even though iron is an excellent catalyst for the $C-H_2$ reaction (7), it appears that in the presence of CO the weight increase due to disproportionation of CO offsets any weight loss due to hydrogasification.

ACKNOWLEDGEMENTS

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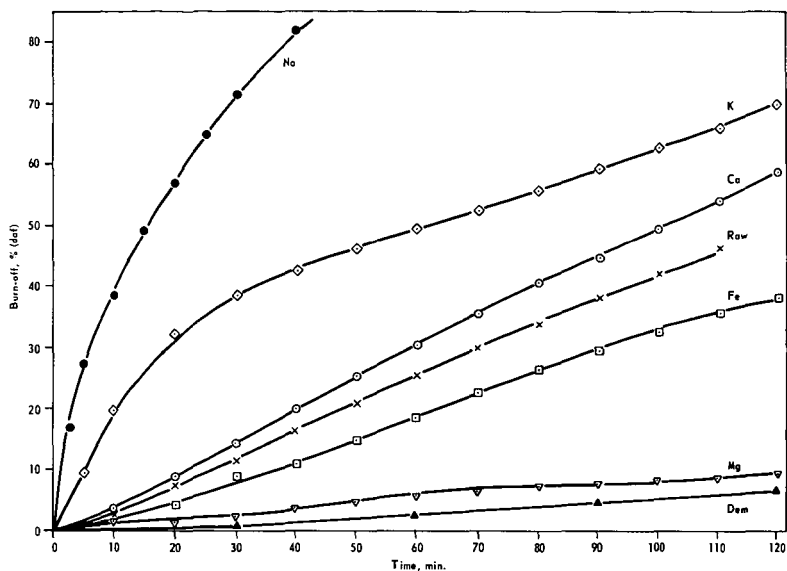


Figure 1. GASIFICATION OF LIGNITE CHARS IN AIR AT 390°C

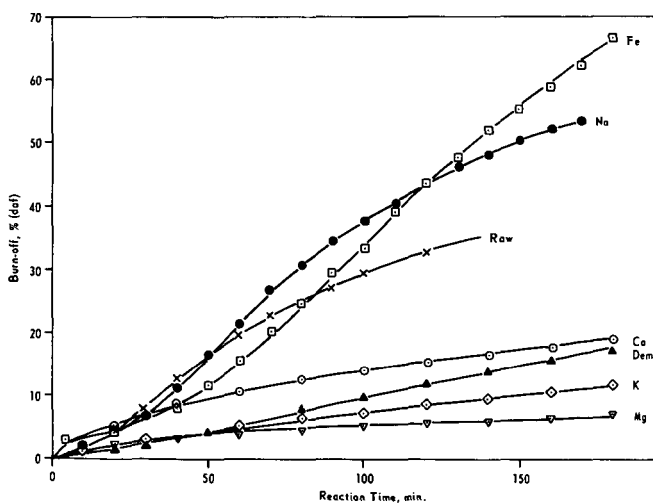


Figure 2. GASIFICATION OF LIGNITE CHARS IN 1 ATM H₂ AT 790°C

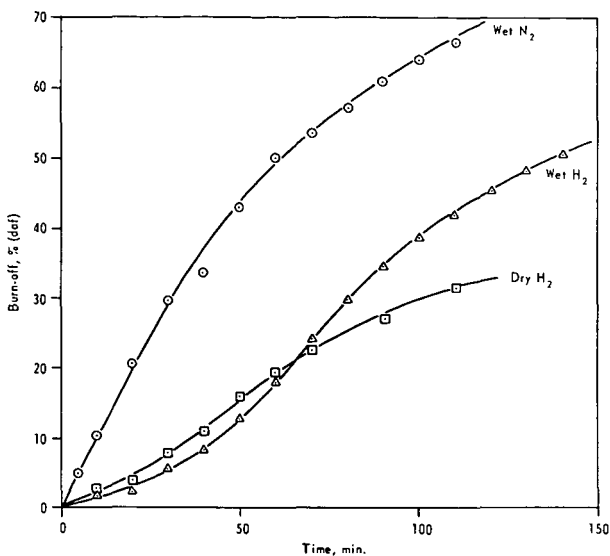


Figure 3. GASIFICATION AT 790°C OF CHAR PRODUCED FROM RAW LIGNITE IN VARIOUS ATMOSPHERES

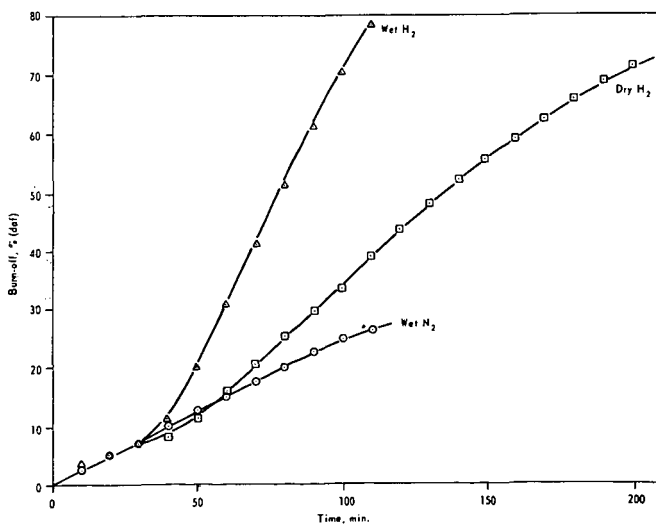


Figure 4. GASIFICATION AT 790°C OF IRON-CONTAINING CHAR IN VARIOUS ATMOSPHERES

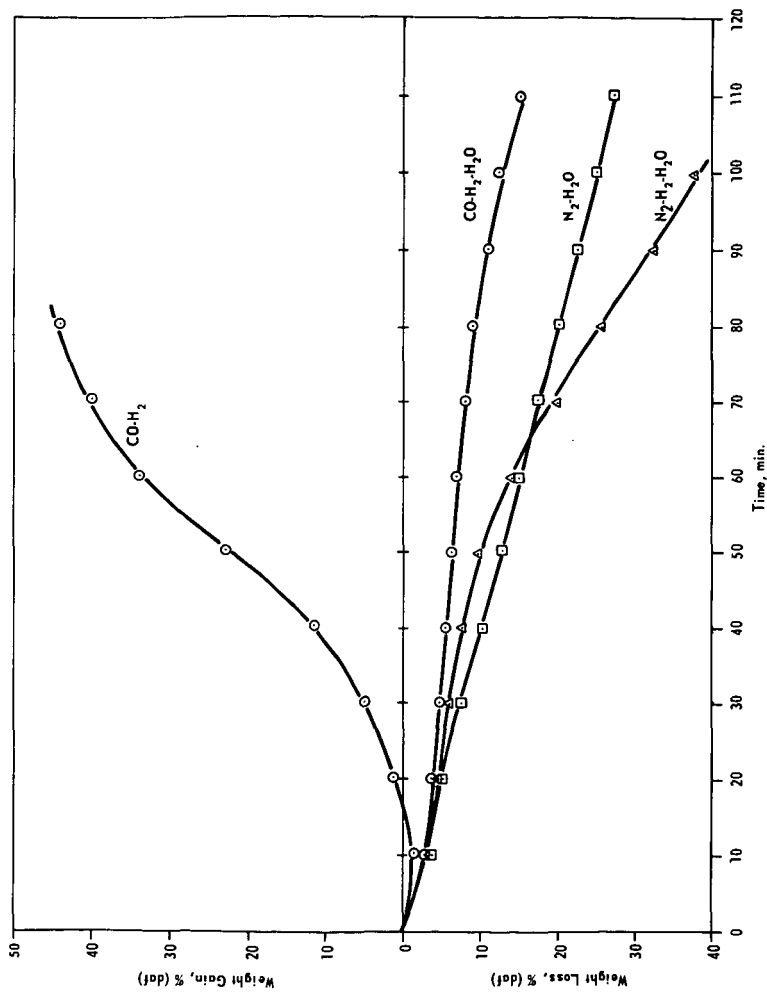


Figure 5. WEIGHT CHANGES FOR IRON-CONTAINING CHARS AT 790°C IN THE PRESENCE OF VARIOUS ATMOSPHERES